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## Modification of Long Range Order in Germanate Glass by Ultra Fast Laser

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### Abstract:

A novel order-disorder phase transition in glasses via ultra fast laser irradiation is first time reported. The Raman spectra of modified region is highly dependent on the polarization of probe beam, indicating the bond orientation at the outer structure of modified region is no longer isotropic and a long-range-order is induced which could be analogue with liquid crystals. The ordered glass phase is not expected from inorganic materials and further investigation is needed.

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## 1. Introduction

In the last decade, ultra fast laser has been widely researched in integrated optics [1-7] and optical data storage [8, 9]. In particular, modification inside glass materials has attracted considerable interest [2-7, 8-13]. Obvious consequences of having high accumulative energy inside a small region by irradiation of femtosecond (fs) laser pulse at a high repetition rate are thermal expansion at the irradiation center and heating above glass transition temperature in the surrounding region [13]. Besides, thermal expansion in the center region induces stress in the surrounding area, which causes densification and a birefringence effect [12].

In the present work, we discover a novel phenomenon that a non-ring-shaped area was observed in the Raman image of the region modified by fs laser. The non-ring shape is due to variation of Raman band intensity in different parts of the laser-modified region. This phenomenon is completely different from our previous study [12] as we just changed the objective lens for fs laser irradiation. Here, we discuss the novel phenomenon and investigate its mechanism.

## 2. Experimental

In our experiments, glass composed of 15Na<sub>2</sub>O-85GeO<sub>2</sub> (mol%) was prepared by

using the traditional melt-quench method. Reagent grade of  $\text{Na}_2\text{CO}_3$ , and  $\text{GeO}_2$  were used as raw materials, mixed and melted in a Pt crucible at 1450 °C for 1 hour in air. Then the melt was casted on a steel plate and quenched. Finally the glass was cut and polished for laser experiment. We used a regenerative amplified 800-nm Ti: sapphire laser (RegA 9000, Coherent Inc.) which emitted 70-fs, 250-KHz mode-lock pulses to irradiate the glass sample. During the experiment the laser pulse was adjusted to 1.4  $\mu\text{J}$  and laser beam was focused 100  $\mu\text{m}$  below the glass surface for 60 seconds, using a 20 $\times$  objective lens with a numerical aperture (NA) of 0.45. The Raman spectra and image were measured using a back-scattering confocal Raman system (Tokyo Instruments; Nanofinder 30) with a 532 nm laser as the excitation source. A 40 $\times$  objective lens with NA of 0.6 was used for Raman measurement, the focal spot size of the 532 nm excitation beam was estimated to be 1  $\mu\text{m}$  in diameter and the pinhole size is 25  $\mu\text{m}$ . The polarization of probe beam of Raman system was measured with a polarizer and a power meter. In addition, the element distribution was measured with an Electron probe micro-analyzer (EPMA, JEOL model JSM-8000).

### 3. Results and discussion

The ellipsoid structure induced around the focal spot (Fig. 1 (a), (b)) is resulted

from refractive index changes caused by fs laser irradiation. The concentric-circle-shape structure was observed. The center of irradiated spot was in melting state and outer structure was still higher than  $T_g$  during fs laser irradiation [13]. The Raman mapping result of the fs-laser-irradiated dot is shown in Fig.1(c). The band peak at  $538\text{cm}^{-1}$  is assigned to symmetric stretching of Ge-O-Ge bonds associated with three-membered ring formation of  $\text{GeO}_4$  tetrahedra, and two high frequency bands at  $821\text{cm}^{-1}$  and  $912\text{cm}^{-1}$  can be assigned to transverse optic/longitudinal optic (TO/LO) splitting of the antisymmetric stretching of Ge-O-Ge bonds within the network [14]. The concentric circles in Raman image of the peak shift is attributed to the variation of Ge concentration caused by element migration, which was confirmed with the EMPA (Fig. 2). However, in all three mappings of the peak intensity we can observe the Raman intensity abnormally decreased at some parts at the outer structure and formed non-ring-shaped region in the mapping. This unexpected result is completely different from that obtained in previous study [12].

Raman spectra in different spots of the irradiated dot are presented in Fig. 3. No peak deformation or peak shift is observed in the Raman spectra from outer structure while the band intensity changes (over 20% at the band of  $538\text{cm}^{-1}$ ), so the Ge-O-Ge bond angle at the outer structure is not affected by strain caused by thermal expansion,

furthermore, no peaks related to crystalline phase was observed. A growth of shoulder at  $450\text{cm}^{-1}$  in the spectra of center is ascribed to the increase of Ge concentration [14]. The variation rates of intensity are different for each Raman bands.

We found the Raman image result is independent of rotation of the sample, indicating the intensity of Raman scattering at outer structure is highly sensitive to the polarization direction of probe beam. Stress birefringence is a possible reason, however, this phenomenon was not observed in our previous work [12], where the stress birefringence of modified area was presented and studied. We also polished the cross section of modified spot to surface, varied the pinhole size of confocal system to improve depth resolution (less than  $2\text{ }\mu\text{m}$ ) and checked the reproducibility. The mapping result is still the same in these circumstances, so we excluded the birefringence to be the reason. Also, the nonhomogenous composition of glass induced by fs laser (Fig. 2) is unjustified to explain the non-ring-shaped image of Raman mapping.

Another reason is that the glass structure was rearranged into an anisotropic state after fs laser irradiation. There are some reports about nano-structuring with fs laser [3, 4], however, these studies are about the central region of focal spot where the plasma interacted with incoming fs laser and the nano-structuring was highly dependent on the polarization direction of fs laser. In our investigation, the Raman image obtained with

different polarization direction of the fs laser had no differences, indicating that the experiment result was independent of the polarization states of fs laser. From the discussions above, the anisotropic property can only be ascribed to the orientation ordering of bonds in germanate glass at outer structure and we present a model of the radial orientation of glass structure as shown in Fig. 4 to explain it, regarding bridging oxygen (BO) as basic vibration unit in analogue with liquid crystal to discuss bond orientation ordering. The probability distribution of BO orientation is described by orientation distribution function (ODF) [15, 16]. From benchmark work done by van Gurp, ODF can be approximated by expressing the ODF as a Fourier transform in terms of the Wigner rotation matrices [15]:

$$f(\alpha, \beta, \gamma) = \sum_{L=0}^{\infty} \sum_{m=-L}^L \sum_{n=-L}^L \frac{2L+1}{8\pi^2} \langle D_{mn}^{L*} \rangle D_{mn}^L(\alpha, \beta, \gamma) , \quad (1)$$

where the indices  $L$ ,  $m$ , and  $n$  represent the symmetry conditions under the rotations about  $\alpha$ ,  $\beta$ ,  $\gamma$ , respectively.  $\langle D_{mn}^{L*} \rangle$  express the complex conjugate of statistical average of the function  $D_{mn}^L(\alpha, \beta, \gamma)$  and could be regarded as order parameter. The exact orientation relationship between principal axes of polarizability of BO and the aligned direction ( $n_z$ ) is unknown, so we can only assume the Placzec vibrational transition polarizability tensor  $\mathbf{R}$  based on BO molecular-fixed Cartesian coordination basis.  $\mathbf{R}$  is symmetric, e.g.  $\alpha_{xy} = \alpha_{yx}$ , because the Placzec approximation applies for transparent

systems when study pure vibrational modes [17]. Rotation transformation could be expressed by a matrix  $\mathbf{T}(\alpha, \beta, \gamma)$ , where  $\alpha, \beta, \gamma$  represent the three Euler angles. Based on the contention proved by Jen *et al.* [16], local field corrections are not needed. So the Raman intensity from a rotated single BO in Fig.4 (b) will be given by [18],

$$I_{BO} \propto |\mathbf{e}_i (\mathbf{T}^{-1}(\alpha, \beta, \gamma) \cdot \mathbf{R} \cdot \mathbf{T}(\alpha, \beta, \gamma)) \cdot \mathbf{e}_s|^2, \quad (2)$$

where  $\mathbf{e}_i, \mathbf{e}_s$  are the polarization vectors of incident and scattered light, respectively. For the illumination-observation geometry of the confocal Raman system illustrated in Fig. 4, the intensity is presented as:

$$I_{obs} = \langle I_{BO} \rangle = \iiint I_{BO} f(\alpha, \beta, \gamma) d\alpha d\beta d\gamma \quad (3)$$

However, the model to describe liquid crystals is not valid for present work since the calculation could not match with the experiment data, as a phase difference  $\phi$  ( $\sim 20$  degree) is presented in Fig. 5. Either uniaxial or mirror symmetry [15] granted liquid crystals a property that the Raman intensity variation with  $\theta$  should be symmetric, as shown in Fig. 5. The experiment result shows that the novel structure of ordered glass is different from liquid crystals. It is possible that the NBO of  $[\text{GeO}_4]$  compromised symmetric property of bond orientation. So the full ODF expression is used and the measured Raman signal is expressed as:

$$I_{obs} \propto A + B\cos 2\theta + C\sin 2\theta + D\cos 4\theta + E\sin 4\theta, \quad (4)$$



where  $\theta$  is the angle between  $n_z$  and polarization direction of probe beam. The coefficient A, B, C, D, and E are related to the orientation distribution and Raman polarizabilities of BO. Unfortunately, quantitatively description of the ordered glass structure is not available due to the limited information we can get, so here we use Eq. 4 as an empirical formula by which the Raman intensity variations could be well fitted with the experiment results (Fig. 5). In the present work we explain unexpected Raman image with the simplest model and demonstrate a new state of matter was discovered.

Additionally, the mechanism of how the long-range-order structure is formed without crystallization in glass requires further investigation. It is commonly known that when polyvinyl alcohol is heated and stretched in a given direction, its long hydrocarbon molecules becoming aligned in the process. In our experiment the ordered glass phase could only be induced in the outer structure where the temperature is not as high as the center during fs laser irradiation. So we propose that the chains of  $[\text{GeO}_4]$  were formed when glass was heated above  $T_g$  but not melted at the outer structure, then these chains got aligned under the stress caused by thermal expansion during the irradiation. In addition, centrifugal temperature gradient and shocking wave were also induced with fs laser irradiation, granting the modified region radial directional properties which cannot be realized with hydraulic method. The aligned structure is

frozen to form the ordered glass by quenching when fs laser stopped.

However, the similarity between germinate glass and polyvinyl alcohol is never expected in known theory and is under further investigation in our group. Besides, the ordered glass could not be created by scanning fs laser beam inside glass. We believe the cooling rate is an important factor. When fs laser stopped irradiation, the cooling rate of glass at surrounding of focal point is much larger than that when laser beam was scanning, so the anisotropic state could be frozen and kept at room temperature. We also propose that the ordered structure could not be induced with an objective lens of high numerical aperture [12] because the strain is too high so that the free space between tetrahedras is not enough for the alignment process.

#### 4. Conclusion

In summary, we observed a non-ring-shaped region in a Raman image of a modified area due to a new state of matter is formed. The existent of such state of matter also indicates bonds orientation of inorganic oxide glass could be controlled by mechanical process, a phenomenon that had so far never been reported or expected. This kind of structure would provide a novel method to control glass structure and property.

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## Figure legends

Figure 1 Optical microscopic and Raman image of fs laser irradiated region. (a), (b), Top and side view optical transmission image of irradiated dot, the arrow indicates fs laser irradiation direction, no voids or bubble is produced as the fs laser is less intensified at the focus spot with a lower NA objective lens. (c), spatial mapping result of relative peak intensity and shift of  $538\text{cm}^{-1}$ ,  $821\text{ cm}^{-1}$ ,  $912\text{ cm}^{-1}$  Raman band, the non-ring-shaped region lies in the outer structure of modified dot. The polarization state of fs laser is arbitrary.

Figure 2 Relative concentration variation illustrated from EPMA result of laser irradiated area

Figure 3 Raman spectra from different spots. The double arrows indicate the polarization direction of probe beam. The angles  $\theta_1 = 54^\circ$   $\theta_2 = 36^\circ$  shows that the non-ring-shaped region neither overlap nor be symmetric about the polarization direction.

Figure 4 Illustration of the anisotropic model induced inside glass. (a), The schematic demonstration of radial orientation arrangement in fs laser modified region. (b),

Rotation of a BO with the reference frame  $n_{x,y,z}$ . The Euler angles  $(\alpha, \beta, \gamma)$  which reflect the orientational degrees of freedom is also defined as shown. (c), (d), The alignment of bridging oxygen after irradiation with respect to laboratory frame. (c) and (d) represent corresponding spots indicated in (a). For consideration of simplification, other elements in glass net work such as Na, Ge and Non-bridging oxygen (NBO) are not represented in the figure and the long-range-order discussed in this work is BO bonding orientation ordering.

Figure 5 Dependence of Raman intensity on  $\theta$  and the fitting curves  $I(\theta)$  derived from calculations. OA is the polarization direction of Raman probe beam (p-polarized). OB is  $30\mu\text{m}$  in length. The intensity of Raman scattering from un-irradiated glass is also presented for comparison of the intensity variations.